Conversion of Non-edible Oil into Biodiesel

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Biodiesel has become more attractive since one decade because of limited fossil resources and increasing demand for diesel. Biodiesel derived from vegetable oils/animal fats triglycerides is a worthy replacement for the hydrocarbon based diesel fuels, because of its multiple benefits, and it can be used in diesel engines without any modification in the existing engines. Transesterification is the most commonly used method for the production of biodiesel from vegetable oils and animal fats in presence of catalytic NaOH/H2SO4 at 70 °C. The transesterification of these oils is affected by the mode of the reaction, molar ratio of the glycerides to alcohol, type and quantity of catalyst, reaction temperature, reaction time and purity of oil and fats. Cost of biodiesel thus obtained is the main obstacle in its commercialization. Efforts are under way in many countries to search options to reduce cost of biodiesel production. Other methods for the preparation of biodiesel with different combination of oils and catalysts have also been summarized. Biodiesel standards provided by different countries are given.

1 Introduction

1.1 Need and Historical Development

Recent petroleum crises, rapidly increasing prices and uncertainties concerning petroleum availability let the scientists work on alternative fuel sources, so vegetable oil as fuel becomes current studies among various investigations. Biodiesel is a liquid; ester-based oxygenated fuel, similar to petroleum based diesel fuel but made from vegetable products; either plant oils or animal fats.

Biodiesel produces favorable effects on the environment, such as decrease in acid rain and emission of CO2, SOx and unburned hydrocarbons during the combustion process. Due to these factors and to its easy biodegradability, production of biodiesel is considered an advantage over that of fossil fuels. The processing of biodiesel has a positive energy balance of roughly 2.5:1, no appreciable difference between biodiesel and diesel — in engine durability or in carbon deposits — have been demonstrated in most laboratory studies. The US Department of Energy estimated that up to 50 per cent of the total diesel fuels consumption could be replaced with biodiesel.

The idea of using vegetable oils as fuel for diesel engines is not new. More than 100 y ago, a brilliant inventor named Rudolph Diesel designed the original Diesel Engine to run on vegetable oil. He used peanut oil to fuel one of his engines at the Paris Exposition of 1900. Transesterification is also not a new process as E Duffy and J Partrick did it in 1853. One of the first uses of transesterified vegetable oil was powering heavy-duty vehicle in the South Africa before World War II. The name biodiesel has been given to transesterified vegetable oil to describe its use as a diesel fuel.

Although vegetable oils may be used directly as fuel in diesel engines without refining, but they present several problems mainly related to viscosity. Vegetable oils have very high viscosity and therefore very difficult to burn in the internal combustion (IC) engines. Chemical conversion of oil with short chain alcohols; such as methanol or ethanol, to its corresponding fatty ester appeared to be the most promising solution to the high viscosity problem. Transesterified vegetable oils or animal fat proved to be the alternative with the best results.

2 Use of Vegetable Oil

2.1 Direct Use of Vegetable Oil

Beginning in 1980, there was considerable discussion regarding use of vegetable oils as a fuel. The concept of using food for fuel, indicating that petroleum should be “alternative” fuel rather than vegetable oils and alcohol. The most advanced work
with sunflower oil occurred in South Africa because of oil embargo. Rapeseed oil was used as a fuel and concluded that, the physical and chemical properties of rapeseed oil as a fuel was very similar to those of diesel fuel, and on a long term basis it can be used in diesel engines\(^5\).

Two severe problems associated with the use of vegetable oils as fuel were oil deterioration and incomplete combustion\(^4\). Polyunsaturated fatty acids were very susceptible to polymerization, and gum formation caused by oxidation during storage or by complex oxidative and thermal polymerization at the higher temperature and pressure of combustion. The gum did not combust completely, resulting in carbon deposits and lubricating oil thickening. One more big problem is high viscosity of the vegetable oil; around 10-15-times more than the diesel fuels\(^5\).

### 2.2 Dilution of Diesel Oil with Vegetable Oils

Blumberg and Ford, made short and long term (200 h) engine performance and emission tests using eight different ratios of cottonseed oil to 2D diesel oil (v/v): 0:100, 30:70, 50:50, 65:35, 80:20, and ratio of transesterified cottonseed oil to 2D diesel fuel, viz, 50:50, 100:0, and 50:50 mix of cottonseed oil and transesterified cottonseed oil\(^5\). They reported that short-term results were more desirable than the long-term results. Long-term tests showed carbon deposit, ash and wear in the combustion chamber and sticky gum content in fuel-line elements. Engine performance tests for 200 h using 25:75 blend (v/v) of soybean and sunflower oil fuel with diesel fuel; showed that engine torque values with mixtures were greater than that with pure diesel operation\(^5\).

Mixtures of degummed soybean oil and No. 2 diesel fuel in the ratios of 1:2 and 1:1 were tested for engine performance and crankcase lubricant viscosity in a John Deere 6-cylinder, 6.6 L displacement, direct-injection, turbocharged engine for a total of 600 h. The lubricating oil thickening and potential gelling existed with the 1:1 mix, but it did not occur with the 1:2 mix. The results indicated that 1:2 mix should be suitable as a fuel for agricultural equipment during periods of diesel fuel shortage or allocation\(^5\).

Sunflower oil and diesel fuel blend (25:75, v/v) showed viscosity of 4.88 cSt at 40 °C, exceeding the maximum allowable value of 4.0 cSt as per the ASTM standard. It was considered not suitable for long-term use in a direct-injection engine. The viscosity of a 25:75 (v/v) high safflower oil and diesel blend was 4.92 cSt at 40 °C. A mixture of 50:50 (v/v) soybean oil and Stoddard solvent (48 per cent paraffins and 52 per cent naphthenes) from Union Oil Co had a viscosity\(^2\) of 5.12 cSt at 38 °C. Both blends of safflower and soybean oil passed the 200 h EMA (Engine Manufacturers' Association) test.

### 2.3 Pyrolysis of Vegetable Oils

Pyrolysis strictly defined; is the conversion of one substance into another by means of heat or by heat with the aid of a catalyst. It involves heating in absence of air or oxygen and cleavage of chemical bonds to yield small molecules. Pyrolytic chemistry is difficult to characterize because of variety of the reaction paths and variety of the reaction products that may be obtained from the reactions that occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The pyrolysis of fats has been investigated for more than 100 y, especially in those areas of the world that lack deposits of petroleum\(^4\).

The first pyrolysis of vegetable oil was conducted in an attempt to synthesize petroleum from vegetable oil. In 1947 a large scale of thermal cracking of tung oil calcium soaps was reported\(^4\). Soybean oil was thermally decomposed and distilled in air and nitrogen sparged in standard ASTM distillation apparatus used safflower oil as a high oleic oil control. The total identified hydrocarbons obtained from distillation of soybean and high oleic safflower oils were 73-77 and 80-88 per cent respectively\(^4\).

Catalytic cracking of copra and palm oils at 450 °C using SiO\(_2\)/Al\(_2\)O\(_3\) as catalysts to produce biofuel have been studied. Rapeseed oil was pyrolyzed to produce a mixture of methyl esters in a tubular reactor at 500-850 °C and in nitrogen\(^4\). A mechanism of thermal decomposition of triglycerides is given below in Figure 1.

The liquid fractions of thermal decomposed vegetable oils are likely to approach diesel fuels\(^5\). The pyrolyzed soyabean oil contained 79 per cent carbon and 11.88 per cent hydrogen. It has low viscosity and a high cetane number compared to the pure vegetable oil. The cetane number of pyrolyzed soyabean oil was enhanced to 43 from 37.9 and the viscosity reduced to 10.2 cSt from 32.6 at 38 °C.
Microemulsion

To solve the problem of high viscosity of vegetable oil, micro-emulsions with solvents such as methanol, ethanol and 1-butanol have been studied. Microemulsions are isotropic, clear, or translucent thermodynamically stable dispersion of oil, water, surfactant, and often a small amphiphilic molecule, called cosurfactant. The droplet diameters in microemulsions ranged from 1-150 nm. A microemulsion can be made of vegetable oils with an ester and dispersant (co-solvent), or of vegetable oils, an alcohol and a surfactant, with or without diesel fuels. Microemulsions because of their alcohol content have lower volumetric heating values than diesel fuels, but the alcohols have high latent heat of vaporization and tend to cool the combustion chamber, which would reduce nozzle coking.

A micro emulsion of methanol with vegetable oils can perform nearly as well as diesel fuels because of lower viscosity than the parent vegetable oil. The use of 2-octanol as an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil has been demonstrated. The viscosity reduced to 11.2 cSt at 25 °C. The reported engine tests on a microemulsion consisting of soybean oil : methanol : 2-octanol : cetane improver (52.7 : 13.3 : 33.3 : 1, v/v) indicated accumulation of carbon around the orifices of injector nozzles and heavy deposits on exhaust valves.

An emulsion of alkali-refined and winterized sunflower oil, 190-proof ethanol and 1-butanol (53, 13.3, 33.4 per cent, v/v) was prepared. This nonionic emulsion was characterized by a viscosity of 6.31 cSt at 40 °C, cetane number of 25 and less than 0.01 per cent an ash content. Lower viscosities and better spray patterns (more even) were observed with an increase of 1-butanol ratio. In a 200 h laboratory screening endurance test, no significant deteriorations in performance were observed, but irregular injector needle sticking, heavy carbon deposits, incomplete combustion and an increase of lubricating oil viscosity were however reported.

3 Vegetable Oil Based Fuels in I.C Engines

3.1 Amidation

It has been reported that diethyl amides of fatty acids show higher cetane numbers than the fatty alcohols or fatty methyl or ethyl esters. Moreover, the chemical transformation of mixtures of triglycerides (oils/fats) to diethyl amides can be easily accomplished in a single chemical process. Thus, amide biodiesel would make a good candidate to incorporate the 5 per cent of biofuels to petrochemical diesel that the European Union plans to achieve for the year 2005. The amidation reaction of fats and oils with diethyl amine was carried out taking into account different experimental procedures, and is summarized in the scheme 1 (ref. 7):
3.2 Transesterification

Transesterification, also called alcoholyis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is used instead of water. This process has been widely used to reduce viscosity of triglycerides. The general transesterification reaction is represented by the equation:

\[
\text{RCOO}^+ + \text{ROH} \rightarrow \text{RCOOR}^+ + \text{ROH}
\]

If methanol is used in the above reaction, it is termed methanolysis and fatty acid methyl esters are generated, which are called biodiesel.

Three consecutive and reversible reactions are believed to occur in the transesterification which are given below:

\[
\text{Triglyceride} + \text{ROH} \rightarrow \text{Diglyceride} + \text{RCOO}^+ \quad \text{(1)}
\]

\[
\text{Diglyceride} + \text{ROH} \rightarrow \text{Monoglyceride} + \text{RCOO}^+ \quad \text{(2)}
\]

\[
\text{Monoglyceride} + \text{ROH} \rightarrow \text{Glycerol} + \text{RCOO}^+ \quad \text{(3)}
\]

The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and finally monoglycerides to glycerol, yielding one methyl ester molecule from each glyceride at each step, when methanol is used in the esterification. A catalyst and excess alcohol are used to increase rate of reaction and to shift the equilibrium to the product side, respectively.

3.3 Supercritical Methanol for Transesterification

Separation of catalysts from the reaction mixture is very difficult. To avoid catalysts in the reaction scientists developed methods for alcoholyis of oils without catalysts. A fundamental study of biodiesel production in supercritical methanol has been carried out. It has been demonstrated that preheating oil to 350 °C and treatment for 240 s in supercritical methanol is sufficient to convert rapeseed oil to its methyl esters. Moreover, while methyl esters produced were basically the same as those obtained in the conventional method with a basic catalyst, its yield was higher in the supercritical methanol method. Transesterification of six vegetable oils (cottonseed, hazelnut kernel, poppyseed, rapeseed, safflowerseed and sunflowerseed) in supercritical methanol without using any catalyst was carried out. A kinetic study in free catalyst transesterification of rapeseed oil was made in sub- and super-critical methanol under different temperatures and reaction times. Runs were made in a bath-type reaction vessel ranging from 200 °C at subcritical state to 500 °C at supercritical state with different molar ratios of methanol to rapeseed oil to determine rate constants of a simple method. The conversion rate of rapeseed oil to its methyl esters increased dramatically in the supercritical state, and reaction at 350 °C was considered as the best, with the molar ratio of methanol in rapeseed oil being 42.

4 Biodiesel Production—Transesterification of Vegetable Oil

4.1 General Method of Manufacturing

Triglycerides are readily transesterified batchwise in the presence of alkaline catalyst at atmospheric pressure and at 60-70 °C with an excess of methanol. The mixture at the end of reaction is allowed to settle. The lower glycerin layer is drawn off, while the upper methyl ester layer is washed to remove entrained glycerol and then processed further. The excess methanol is recovered in the condenser.
sent to a rectifying column for purification and recycled.

4.2 Effect of Different Parameters on the Production of Biodiesel

4.2.1 Impurities

Impurities present in oils also affect conversion level. For alkali catalyzed transesterification, the glycerides and alcohol must be substantially anhydrous as water causes a partial reaction change to saponification, which produces soap. The soap consumes the catalyst, reduces the catalytic efficiency, as well as causing an increase in viscosity, the formation of gels, and difficulty in achieving separation of glycerol. Under the same conditions 67-84 per cent conversion of crude vegetable oils into esters can be obtained compared with 94-97 per cent when refined oils are used. The free fatty acids in native oils interfere with the catalyst. However, under conditions of high temperature and pressure this problem can be overcome. The effect of free fatty acids and water on transesterification of beef tallow with methanol was investigated. The results showed that the water content of beef tallow should be kept below 0.06 per cent (w/w) and free fatty acid be kept below 0.5 per cent (w/w) in order to get the best conversion. Water content was a more critical factor in the transesterification process than were the free fatty acids. The maximum content of free fatty acids confirmed the results of earlier work.

4.2.2 Alcohol Type

Methanol and ethanol are most commonly used for transesterification of vegetable oils and fats but other alcohols can also be used. It has been reported that yield of alcohol esters was the highest for methanol, as methanol is the shortest-chain alcohol and more reactive to oil with the added advantage of alkali catalysts being easily soluble in it.

4.2.3 Reactants Ratio

Very important factor affecting the yield of ester is the molar ratio of alcohol to vegetable oil. The stoichiometry of the transesterification reaction requires 3 mol of alcohol per mole of triglyceride to yield 3 mol of fatty esters and 1 mol of glycerol. The reaction being reversible in nature, it is necessary to use either a large excess of alcohol or to remove one of the products from the reaction mixture to favourably shift reaction to the product side. The second option is preferred wherever feasible, since in this way, the reaction can be driven to completion. When 100 per cent excess methanol is used, the reaction rate is at its highest. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields greater than 98 per cent on weight basis. Transmethylated palm oil at 70 °C in toluene with sodium methoxide as catalyst resulted in the conversion that increased with molar ratio of methanol. A molar ratio of 6:1 was used for transesterification of beef tallow with methanol. Zhang reported 80 per cent recovery of esters by tallow weight in laboratory. Methanol present in amounts above 1.75 equivalents tended to prevent gravity separation of glycerol, thus adding more costs to the process.

4.2.4.1 Basic Catalyst — Catalysts are classified as alkali, acid, or enzyme. Alkali-catalyzed transesterification is much faster than other type of the catalysts. Alkalis include sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide, sodium amide, sodium hydride, potassium amide, and potassium hydride. Sodium hydroxide was also chosen to catalyze the transesterification as it is cheaper. Ester conversions at the 6:1 ratio for 1 per cent NaOH and 0.5 per cent NaOCH3 were almost the same after 60 min. NaOH and NaOCH3 reached their maximum activities at 0.3 and 0.5 per cent (w/w, beef tallow basis), respectively.

4.2.4.2 Acid Catalyst — However, if a glyceride has a higher level of free fatty acids (FFA) content and more water, then acid-catalyzed transesterification is suitable. The acid could be sulfuric, phosphoric, hydrochloric or organic sulfonic acid. Acid catalyzed methylation is energy sensitive because it is usually conducted at high temperature. Palm oil with 3 per cent H2SO4 gives highest yield of 78 per cent methyl esters at 23:1 mol/mol.

4.2.4.3 Bio Catalyst — As described above that the catalysts used in the biodiesel production are alkali and acid, but the recovery of catalysts are very difficult. It can affect the process economically as well as ecologically. Several reports describe enzymic
4.2.6 Reaction Temperature

70 °C, at atmospheric pressure. These mild reaction conditions, however, require the removal of free fatty acids from the oil by refining or pre-esterification. Therefore, the degummed and de-acidified feedstock is used at these conditions. The pretreatment is not required if the reaction is carried out under high pressure (9000 kPa) and temperature (240 °C). Under these conditions, simultaneous esterification and transesterification take place. The maximum yield of esters occurs at 60-80 °C, with molar ratio of alcohol to oil of 6:1. Further increase in temperature is reported to have a negative effect on the conversion. The butanolysis and methanolysis of soybean oil were studied at different temperatures in the presence of acidic and alkaline catalysts. These studies indicated that transesterification can proceed satisfactorily at ambient temperature in the case of alkaline catalysts.

4.2.7 Stirring effect

In the transesterification reaction, the reactants initially form a two-phase liquid system. The reaction is diffusion-controlled and poor diffusion between the phases results in a slow rate. As methyl esters are formed, they act as a mutual solvent for the reactants and a single-phase system is formed. The mixing effect is most significant during the slow rate region of the reaction. As the single phase is established, mixing becomes insignificant. The understanding of the mixing effects on the kinetics of the transesterification process is a valuable tool in the process scale-up and design. Conversion of soybean oil as a function of time and stirring, after optimization of the reaction conditions—methanol:oil ratio of 7.5:1, at 60 °C; with 1 per cent sodium methoxide, at 600 rpm — 90 per cent conversion was noted after 30 min, while at 360 rpm, only 20 per cent conversion was obtained after 8 h.

5 Biodiesel Standards

Biodiesel is produced in quite differently scaled plants from vegetable oils of varying origin and quality. Therefore, it was necessary to install a standardization of fuel quality to guarantee engine performance. Therefore, in 1992, Austria was the first country in the world to define and approve the standards for the rapeseed oil methyl esters as diesel fuel (O-NORM, 1992). As standardization is prerequisite for the successful market introduction and penetration of biodiesel, standards or guidelines for defining the quality of biodiesel have also been defined in other countries, like Germany (DIN V...
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